

Vapor-Phase Association of *N*-Aliphatic Carboxylic Acids

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Abstract

*Vapor-phase association greatly affects the pure-component properties of carboxylic acids. This study uses Density Functional Theory (DFT) calculations to quantify the size and distribution of oligomers present in *n*-aliphatic carboxylic acid vapors and includes recommendations on how this information may be used in modeling the acids. Acids from C2 to C6 were studied using B3LYP/6-31++G(2d,p).*

New association equations were developed for the acids from C4 to C10 using the family trend obtained from the B3LYP calculations,. Dimers were found to be the dominant oligomer in the vapor phase, with little association of larger oligomers. Association in acids larger than C10 is negligible at modest temperatures and pressures.

There is a notable difference in the dimerization enthalpy between acids with an even number of carbon atoms and those with an odd number of carbon atoms.

Introduction

It is a well-known fact that carboxylic acid molecules tend to associate in the vapor phase, forming oligomers consisting of two or more acid molecules held closely together by hydrogen bonds. This association requires special treatment when dealing with the physical properties of these compounds. It is difficult to measure and interpret carboxylic acid vapor-phase data because of difficult sample purification and unwanted reactions at temperatures of interest. These difficulties have led to a scarcity of reliable data, especially PVT data, for carboxylic acids. This study was undertaken to better understand vapor-phase association in the *n*-aliphatic carboxylic acid family.

It is common practice to represent the vapor-phase behavior of carboxylic acids using an equation of state in conjunction with an equilibrium equation for dimerization. This practice assumes that the dimer is the predominant oligomer in carboxylic acid vapor. Some studies suggest that higher-order oligomers may also play a significant role in the vapor-phase behavior of the acids. The current study seeks to clarify this issue.

Ab initio and density functional theory (DFT) calculations of *n*-aliphatic carboxylic acids have only recently been explored as a method of understanding vapor-phase association [1-3]. These methods can be used to evaluate the enthalpies and

entropies of association, the relative stability of various oligomers, and the equilibrium constants for the interconversion between the stable molecular forms. These computed values can be used to help interpret experimental data, but they also allow exploration of association phenomena in larger molecules where data are unavailable or inadequate.

More specifically, Wolbach and Sandler performed *ab initio* and DFT calculations on formic, acetic, and propionic acid and their dimers. Their results showed that current computational capabilities can be used to effectively model carboxylic acid dimerization, but they did not study higher-order oligomers. The current study extends their work to the study of larger oligomers and longer-chain acids to determine the relative amounts of various oligomers likely to be present in the acid vapor.

Discussion of Results

The two calculation methods used by Wolbach and Sandler were also selected for this study. The first method used was HF/6-31G(d,p). The second method was the more computationally intensive B3LYP/6-31++G(2d,p). These methods were selected because they provide a good balance between CPU time and accuracy, and they permit comparison to the previous work for validation purposes.

All calculations were performed using the Gaussian 98 suite of computational chemistry programs [4], using Unichem [5] as a graphical interface for the calculations. Geometry optimizations were performed with the same calculation method as the

frequency calculations. Vibrational frequencies from the HF calculations were scaled by 0.8929 and frequencies from the B3LYP calculations were scaled by 0.9613 as recommended by Foresman and Frisch [6]. All bond angles and distances were allowed to relax during the optimizations.

The calculation methods were first validated by comparing the calculated results to experimental data for acetic acid and to the calculations of Wolbach and Sandler. Following this validation, the B3LYP method was used to examine oligomers larger than the dimer in acetic acid. Longer-chain *n*-aliphatic acids were then studied using the same methods.

Validation of Calculation Methods

Table 1 shows the results obtained for acetic acid enthalpies and entropies of dimerization in comparison to experimental values and those obtained by Wolbach and Sandler.

Table 1 shows that the HF calculations provide reasonable estimates for the dimerization properties of acetic acid. The HF calculations performed in this work and those performed by Wolbach and Sandler are in close agreement with each other, as expected, but significant differences exist between the B3LYP calculations of this work and those of Wolbach and Sandler. Our B3LYP results show a marked refinement over the HF calculations in comparison to the experimental results. The good agreement

between the B3LYP results in this study and the experimental values provides good credibility for the calculated results. It is not clear why our B3LYP results differ from those of Wolbach and Sandler, but the improved accuracy is encouraging.

Using the calculated thermodynamic parameters, the equilibrium constant was obtained from Equation 1. Values obtained for K were then fit to Equation 2 in order to provide a convenient temperature-dependent dimerization equation. Gmehling et al. [9] have collected most of the reliable PVT data for the carboxylic acids and reduced the data to useful temperature-dependent dimerization equilibrium equations. Unfortunately, the equations for the acids C4 and above were extracted from a single paper [10] which only measured a few data points for the C4 and C7 acids, and the accuracy was questioned by the authors of the study. Dimerization equations for the acids from C4 to C10 were extrapolated and interpolated by Gmehling et al. using these inaccurate measurements. For this reason Gmehling et al.'s dimerization equations for the C2 and C3 acids are helpful for validating the calculation method of the current study, but the equations for the larger acids are less useful. Acids larger than C2 are further discussed later in this paper. Table 2 compares our calculated results for the C2 acid equilibrium equation coefficients to values reported by Gmehling et al. and calculated by Wolbach and Sandler.

$$K_2 = \exp(-\Delta H + T\Delta S) \quad (1)$$

$$\ln K_2 = A + \frac{B}{T} \quad (2)$$

There is excellent agreement between our B3LYP values for K_2 and the experimental measurements, further validating the use of B3LYP in the examination of larger acids and larger oligomers. The “B” coefficient, which is related to the ΔH of association and represents the temperature functionality of the equilibrium constant, is predicted particularly well by the B3LYP.

Figure 1 shows a plot of the Gmehling et al. equilibrium constant expression along with the expression generated from this work’s B3LYP calculations. The temperature range represented is from 275 K to 600 K. The two equations nearly overlap across the entire temperature range. The B3LYP equation is offset only slightly from the Gmehling et al. equation. This small offset causes a difference of less than 5% when the equations are used to calculate the mole fractions of monomer and dimer present at 1 atm. The B3LYP equation predicts about 4% more monomer present than the Gmehling et al. equation from 275 to 600 K. This agreement falls within the experimental error associated with experimental measurements. We assume that the accuracy of comparable B3LYP calculations for the C3 to C6 acids studied here should be approximately the same, perhaps within about 5%.

Vapor-Phase Oligomers

Various acetic acid oligomers were examined using B3LYP calculations. Acetic acid was chosen because the small size of the molecule allows reasonable calculation times and because more physical measurements exist for acetic acid than the other *n*-aliphatic acids. Oligomers present in acetic acid vapor should also be present in the vapor phase of the larger acids. Thus, acetic acid was used to identify important oligomers and hopefully rule out some oligomers in order to decrease the number of calculations necessary for the larger acids. Dimer results are presented first, followed by trimer, tetramer, and hexamer results.

Dimer Results

B3LYP calculations were used to determine accurate temperature-dependent dimerization constant equations for acetic acid as discussed in the previous section. At low enough pressures where the fugacity coefficients are unity, the vapor-phase equilibrium constant for the dimer, K_2 , can be written in terms of the monomer and dimer mole fractions, y_m and y_d , respectively, as Equation 3, where P is the total pressure. This equation can be solved, using $y_d + y_m = 1$ to obtain the equilibrium compositions.

$$K_2(T) = \frac{y_d}{y_m} P \quad (3)$$

Using B3LYP results for K_2 at 400 K and 1 bar, $y_d = 0.5$. The dimer is thus seen to be a significant species in the vapor phase even at modest temperatures and pressures. Figure 2 shows the vapor component mole fractions as a function of temperature at $P = 1$ bar, and Figure 3 shows the vapor mole fractions as a function of pressure at $T = 350$ K. The dimer fraction decreases with increasing temperature and increases with increasing pressure. As pressure approaches zero, the fraction of associated species approaches zero.

Dimer geometry was also examined. The stable form of the dimer for B3LYP/6-31++G(2d,p) consists of a ring structure in which all molecules in both acid groups (COOH) are coplanar. The ring structure of the acetic acid dimer is shown in Figure 4.

Trimer Results

The acetic acid trimer was also examined. The stable trimer geometry consists of a ring structure in which all the molecules of the acid groups are coplanar. A fit of the trimerization constants calculated using B3LYP yielded an A value of -29.102 and a B value of $9,127.3$ K. Vapor mole fractions of trimer were calculated from the equilibrium expression analogous to Equation 2. The trimer mole fraction was found to be negligible. Even at a low temperature of 300 K and a high pressure of 10 bar, where the trimer fraction is expected to be fairly high, the calculated mole fraction of trimer present was 0.0004. At lower pressures and higher temperatures the trimer fraction is even smaller.

The small amount of trimer present is partially attributed to the large negative entropy (relative to the dimerization entropy) associated with the increased order of trimer formation. The calculated entropy of trimerization at 298 K is $-244.5 \text{ J/mole}\cdot\text{K}$ while the calculated entropy of dimerization at 298 K is $-146.3 \text{ J/mole}\cdot\text{K}$. This entropy difference results in a substantial difference in Gibbs energies (-17.3 kJ/mole for the dimer versus -3.73 kJ/mole for the trimer at 298 K). As the trimer mole fraction was found to be insignificant in acetic acid, the trimer was not investigated in the larger acids.

The relative strength of the hydrogen bonds in the oligomer structures can be determined by examining the association enthalpies of the oligomers. The enthalpy of dimerization calculated using B3LYP theory at 298 K is -30.4 kJ per mol of hydrogen bonds while the enthalpy of trimerization at 298 K is -25.5 kJ per mol of hydrogen bonds. The smaller magnitude of the trimerization enthalpy indicates that the hydrogen bonds in the trimer are weaker than those in the dimer. The weakening of the hydrogen bonds in the trimer is attributed to strains on the hydrogen bonds caused by the trimer geometry.

Tetramer Results

Several possible tetramer geometries were examined, including a lamellar structure of the type postulated by Ritter and Simons [11]. The stable form of the

tetramer was a ring structure with coplanar acid groups similar to the dimer and trimer, but with strained hydrogen bonds similar to the trimer geometry.

The calculated enthalpy of association at 298 K for the tetramer is -26.0 kJ per mole of hydrogen bonds. The calculated entropy of association for the tetramer at 298 K is -403.3 J/mole·K. As the number of associated molecules in an oligomer increases, the negative entropy of association becomes increasingly prohibitive to oligomer formation.

The temperature-dependent tetramerization constant equation has an A value of -49.63 and a B value of $12,872$ K. This equation yields a K_4 value of 0.0016 at 298 K. This value is 3 orders of magnitude smaller than the trimerization constant at 298 K and yields tetramer vapor fractions even smaller than those of the trimer. Since it was previously determined that the trimer fractions were insignificant in calculating carboxylic acid vapor properties, the effect of the tetramer was also discounted. The tetramer was not studied in acids longer than C2.

Hexamer Results

The hexamer has been postulated as a likely oligomer in carboxylic acid vapor. A calculation at the B3LYP level would have been computationally infeasible for the hexamer so a calculation was performed using HF/6-31G(d,p). Though probably not as

accurate as the B3LYP calculations, this calculation can be used to give the geometry and approximate thermodynamic parameters.

A planar ring was used as the starting geometry for the hexamer calculation but surprisingly the ring proved to be an unstable geometry. The stable geometry determined for the hexamer is a mobius strip.

The enthalpy of association determined was -31.1 kJ per mole of hydrogen bonds and the entropy was -689.3 J/mole·K. The thermodynamic parameters yielded an association constant of 0.0006 at 298 K. Though these calculations are not very precise, they are probably within an order of magnitude of what the B3LYP calculations would yield. This would produce a hexamer fraction of about the same magnitude as the tetramer fraction. For this reason the hexamer was considered insignificant in determining vapor-phase properties for the carboxylic acids and the hexamer was not examined for acids longer than C2.

Association in Acids with Longer Carbon Chains

Based on the examination of acetic acid oligomers detailed in the previous section, dimers were considered the only important oligomers in the vapor phase of the carboxylic acids. This agrees with the findings of Curtis and Blander [7], who used vapor thermal conductivity measurements to determine which oligomers are present in

acetic acid. Thermal conductivity measurements are very sensitive to the presence of oligomers larger than the dimer. In the current study, only dimers were examined in the acids larger than C2As before, B3LYP/6-31++G(2d,p) calculations were used to determine geometries and thermodynamic properties. The results of all acids studied (C2-C6) are presented together in order to determine the family trend of association constants.

The planar ring structure exhibited in the acetic acid dimer is the stable geometry for all the acid dimers studied. Table 3 shows the enthalpies and entropies of association calculated for each of the acids studied.

Table 4 shows the parameters for the fit of each acid's dimerization constant to Equation 1 as well as association constant values at 298 K.

It is often useful to exclude C1 and C2 from a family data set in examining family trends since they often do not conform. If C2 is excluded from this data set, the enthalpies of the set exhibit a pattern corresponding to odd and even carbon numbers. The odd carbon-number atoms have an enthalpy of association near -64 kJ per mole of dimers while the even carbon-number atoms have an enthalpy of association near -57 kJ per mole of dimers. The calculated enthalpies are repeatable to ± 2.0 kJ/mol and the entropies are repeatable to ± 2.0 J/mol·K. The enthalpy of association corresponds to the slope of the $\ln K_2$ versus $1/T$ plot, so that the odd and even carbon numbered acids

separate on the plot into two different groups as shown in Figure 5. As can also be seen in Figure 5, the dimerization constant decreases with increasing carbon number, indicating less association with larger acids.

In order to be more certain that this odd/even grouping phenomenon was not an artifact of the level of theory and basis set chosen for this study, additional calculations were run for these acids using HF/6-31G(d,p). These calculations, while not as accurate as the DFT used previously, also showed the same odd/even grouping of association constants. A plot of $\ln K_2$ versus $1/T$ as determined from the HF calculations is shown in Figure 6.

As previously mentioned, very few reliable experimental data are available for association of acids larger than C2. Some data are available for propionic acid and one paper is available in which the association in the C4 and C7 acids is reported. Unfortunately, the study of the C4 and C7 acids is not very reliable.

Gmehling et al. report coefficients for the dimerization constant of propionic acid which are based on reliable vapor density data. The $\ln K_2$ versus $1/T$ plot of the Gmehling et al. equation for propionic acid compares very favorably with the equation derived from the B3LYP calculations of this study. This plot is shown in Figure 7. Table 5 shows the Gmehling et al. and B3LYP parameters fitted to Equation 2 for propionic acid as well as the thermodynamic parameters associated with these fits.

Although the numerical values from the B3LYP calculations for the dimerization of butyric acid do not agree with the Gmehling et al. values, as shown in Figure 8, the temperature dependence (slopes), or enthalpies of association are in excellent agreement. The agreement between the slopes for the C3 and C4 acid dimerization equations and the best-fit experimental data indicates that the limited experimental data also partitions into the odd/even groups shown in Figure 5.

The association constants derived from B3LYP calculations in the current work provide a solid basis for approximating association constants of acids larger than can be handled directly with DFT calculations. Association equations for C2 to C6 were obtained directly from the B3LYP calculations, but we have also extrapolated the results empirically to the acids from C7 to C10. To do so, we assume constant average ΔH of association within the odd/even groups and that the decrease in K_2 with carbon number, at fixed T , is linear. Table 6 shows the thermodynamic association properties that result from this extrapolation.

It has previously been conjectured that vapor-phase association is negligible in acids larger than C10. Based on the current estimates the mole fraction of dimer in the C10 vapor at 400 K and 0.00380 bar (the saturated vapor pressure at 400 K) is 0.0004. The fraction of C10 dimer calculated at the normal boiling point (543.15 K and 1 bar) is 0.001. At higher temperatures, even less of the dimer should be present. At a temperature of 543.15 K and a pressure of 10 bar, the calculated mole fraction of dimer is

0.01. Based on these calculations, it seems reasonable to state that dimerization is negligible under most normal conditions for acids larger than C10.

Conclusions

This *ab initio*/DFT study focused on defining the relative amounts of various oligomers thought to be present in the vapor phase of carboxylic acids. Based on the results, a monomer-dimer model is recommended. Larger oligomer formation is precluded by the large negative entropy required for the formation of oligomers beyond the dimer. The dimer was found to form a particularly stable ring geometry.

The acids show a previously unobserved separation into groups based odd or even carbon numbers. The association constants of the two groups behave in a similar manner but the ΔH of association is different for the two groups, probably due to a slightly different charge distribution among the odd and even carbon-number groups.

The association equations recommended here provide reliable estimates for carboxylic acids from C2-C10. The association equations for C2 and C3 are in close agreement with available experimental values, but for acids C4 and larger, reliable PVT data are unavailable.

LIST OF SYMBOLS

K_2	Dimerization constant
ΔH	Enthalpy of association
T	Temperature
ΔS	Entropy of association
A	Fitted constant
B	Fitted constant
y_d	Dimer vapor mole fraction
y_m	Monomer vapor mole fraction
P	Pressure

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TABLES

**Table 1. Acetic Acid Dimerization Properties
Current Work vs. Previous Work**

Quantity	Experimental Value	Wolbach and Sandler HF	Wolbach and Sandler B3LYP	This Work HF	This Work B3LYP
ΔH (300 K, kJ/mol)	-61.1±2.1 [7] -59.5±2.9 [8]	-58.28 [3]	-58.45 [3]	-58.24	-60.87
ΔS (300 K, J/mol·K, 1 bar)	-146±8.4 [7]	-142.6 [3]	-151.1 [3]	-142.6	-146.2
ΔH (373 K, kJ/mol)	-61.29±3.3 [7]	-57.57 [3]	-57.99 [3]	-57.53	-60.42
ΔS (373 K, J/mol·K, 1 bar)	-148.6±3.3 [7]	-140.8 [3]	-150.1 [3]	-140.4	-144.9

**Table 2. Acetic Acid Dimerization Equation Coefficients
This Study vs. Wolbach and Sandler**

Quantity	Gmehling et al.	Wolbach and Sandler HF	Wolbach and Sandler B3LYP	This Work HF	This Work B3LYP
A(unitless)	-17.362	-17.466	-18.606	-17.021	-17.512
B(K)	7,290	7,112	7,169	6,971	7,299
K_2(298 K)	1,213	602	233	582	1,070

Table 3. Acid Dimerization Thermodynamic Properties by Carbon Number

	C2	C3	C4	C5	C6
Enthalpy kJ/mol dimers	-60.69	-64.95	-57.07	-63.30	-57.56
Entropy J/mol dimers·K	-145.6	-156.6	-146.9	-154.5	-153.1

Table 4. Acid Dimerization Equation Constants by Carbon Number

	C2	C3	C4	C5	C6
A(unitless)	-17.512	-18.829	-17.664	-18.586	-18.411
B(K)	7,299	7,812	6,864	7,614	6,923
K₂(298 K)	1,070	1,606	214	1,052	124

Table 5. Gmehling et al. vs. B3LYP Parameters for C3 Association

	A (unitless)	B (K)	Enthalpy (kJ/mole of dimers)	Entropy (J/mole of dimers·K)
Gmehling et al.	-18.334	7,636	-63.49	-152.4
B3LYP	-18.829	7,812	-64.95	-156.6

Table 6. Extrapolated Association Parameters for C7-C10

	A (unitless)	B (K)	Enthalpy (kJ/mole of dimers)	Entropy (J/mole of dimers·K)
C7	-18.909	7,713	-64.13	-157.2
C8	-18.989	6,894	-57.32	-157.9
C9	-19.231	7,713	-64.13	-159.9
C10	-19.568	6,894	-57.32	-162.7

LIST OF FIGURE CAPTIONS

Figure 1. Acetic Acid Equation 2 Equilibrium Expressions from Gmehling et al. (●) and from This Work's B3LYP Calculations (□)

Figure 2. Acetic Acid Monomer (---) and Dimer (—) Component Mole Fractions at 1 bar

Figure 3. Acetic Acid Monomer (- - -) and Dimer (—) Component Mole Fractions at 350 K

Figure 4. Ring Structure of the Acetic Acid Dimer

Figure 5. Equation 2 Equilibrium Expressions of the Acids (B3LYP calculations, C3 (○), C4 (Δ), C5 (□), C6 (x))

Figure 6. Equation 2 Equilibrium Expressions of the Acids (HF/6-31G(d,p), C3 (○), C4 (Δ), C5 (□), C6 (x))

Figure 7. Propionic Acid Equation 2 Equilibrium Expressions from Gmehling et al. (●) and from This Work's B3LYP Calculations (□)

Figure 8. Butyric Acid Equation 2 Equilibrium Expressions from Gmehling et al. (●) and from This Work's B3LYP Calculations (□)

FIGURES

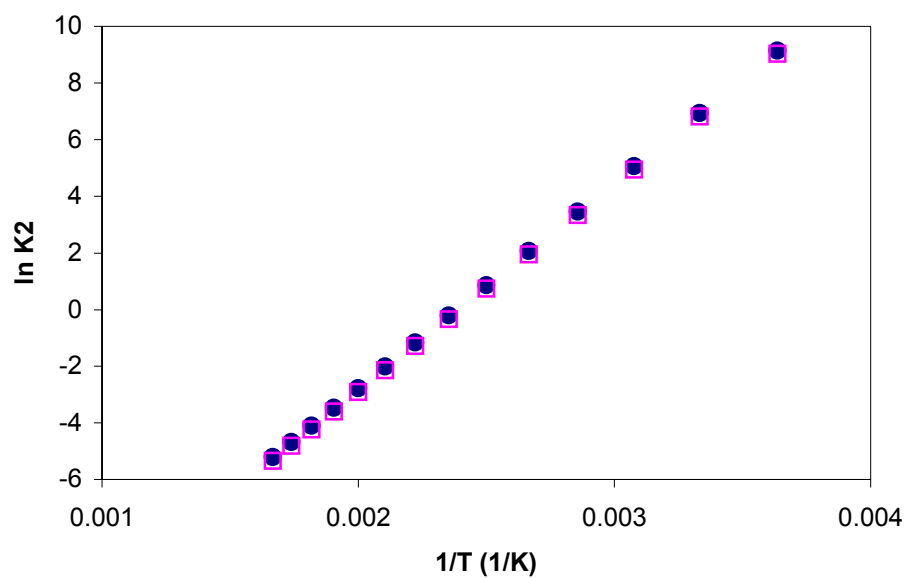


Figure 1. Acetic Acid Equation 2 Equilibrium Expressions from Gmehling et al. (●) and from This Work's B3LYP Calculations (□)

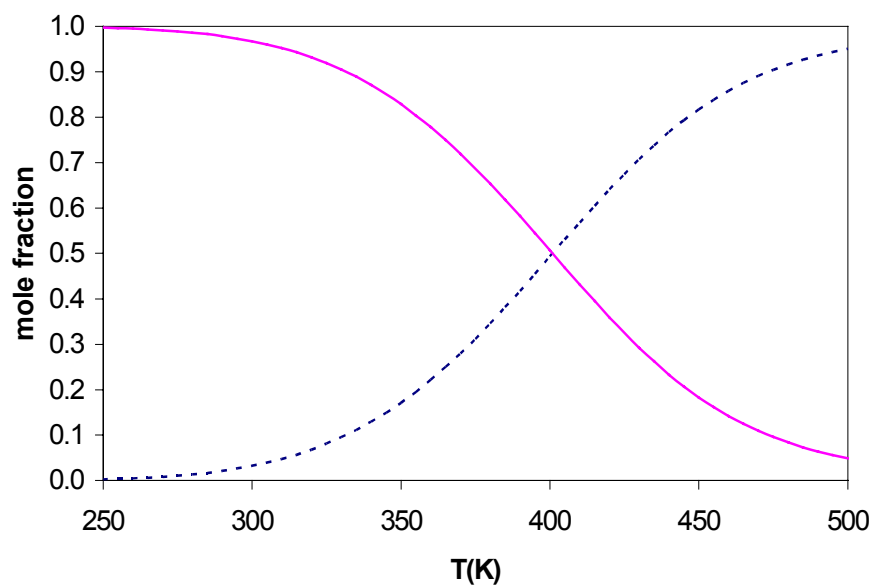


Figure 2. Acetic Acid Monomer (---) and Dimer (—) Component Mole Fractions at 1 bar

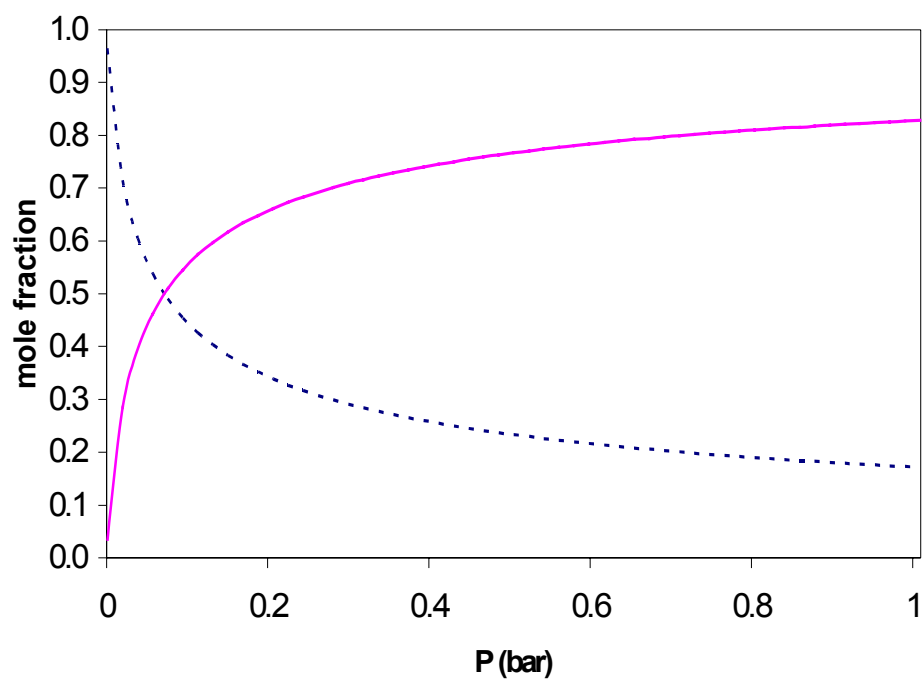


Figure 3. Acetic Acid Monomer (- - -) and Dimer (—) Component Mole Fractions at 350 K

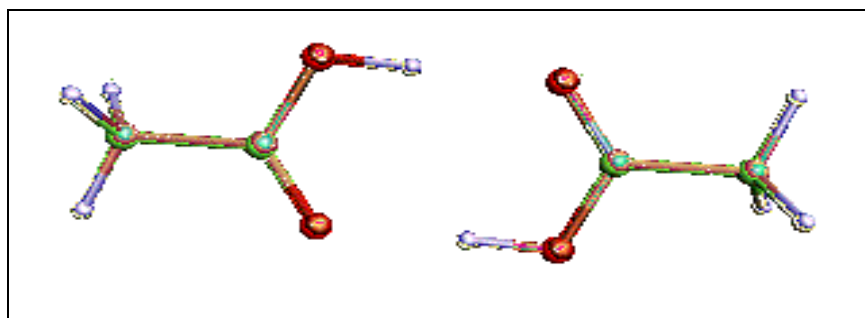


Figure 4. Ring Structure of the Acetic Acid Dimer

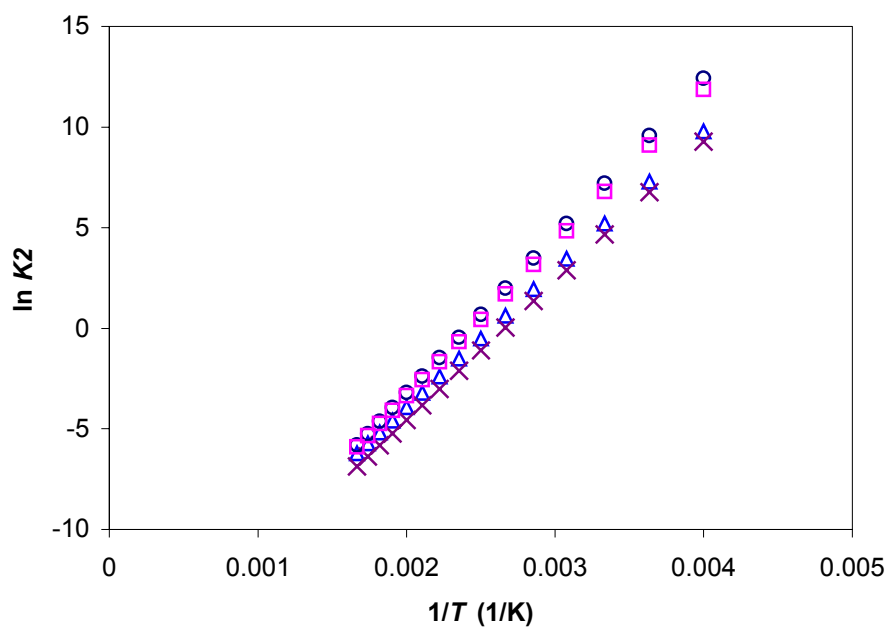


Figure 5. Equation 2 Equilibrium Expressions of the Acids (B3LYP calculations, C3 (\circ), C4 (Δ), C5 (\square), C6 (\times))

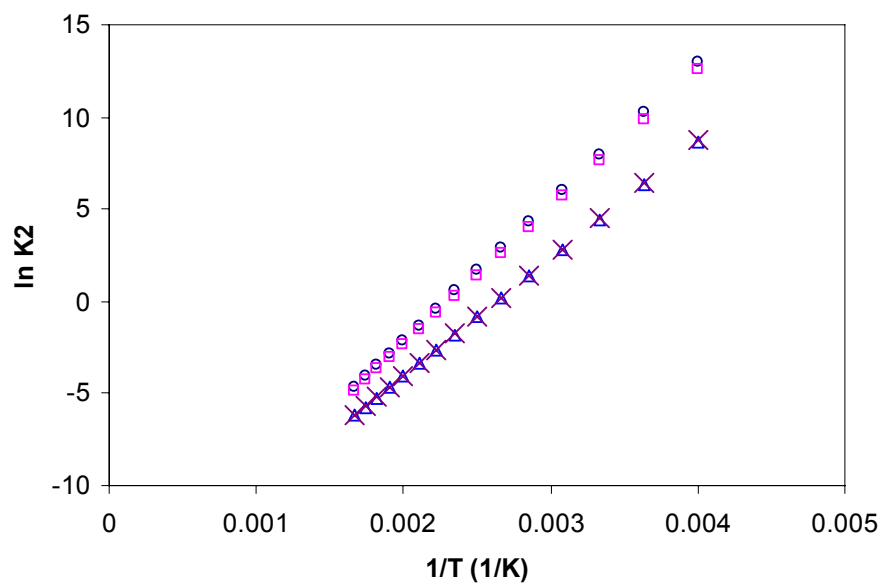


Figure 6. Equation 2 Equilibrium Expressions of the Acids (HF/6-31G(d,p), C3 (\circ), C4 (Δ), C5 (\square), C6 (\times))

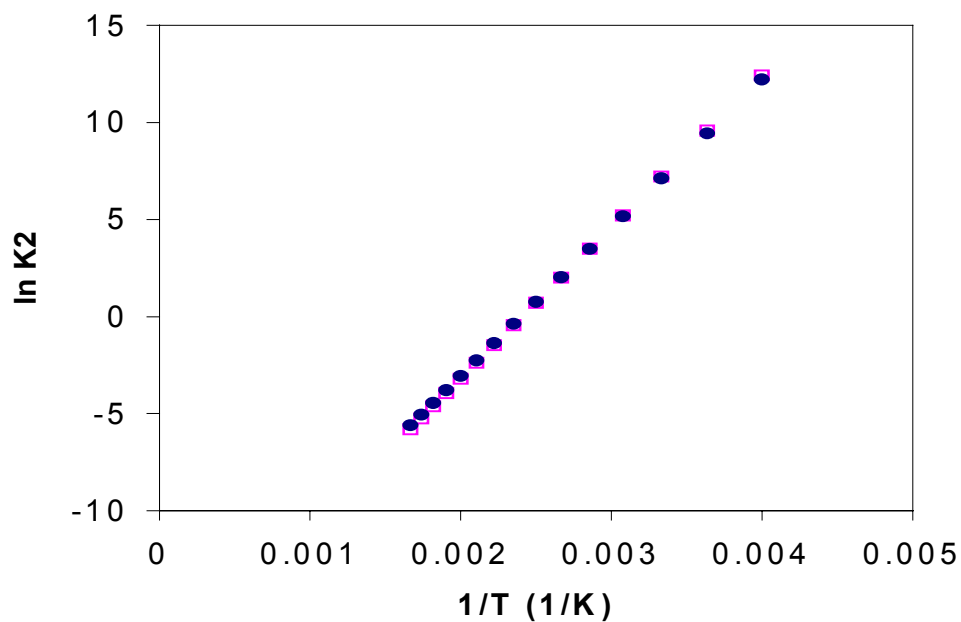


Figure 7. Propionic Acid Equation 2 Equilibrium Expressions from Gmehling et al. (●) and from This Work's B3LYP Calculations (□)

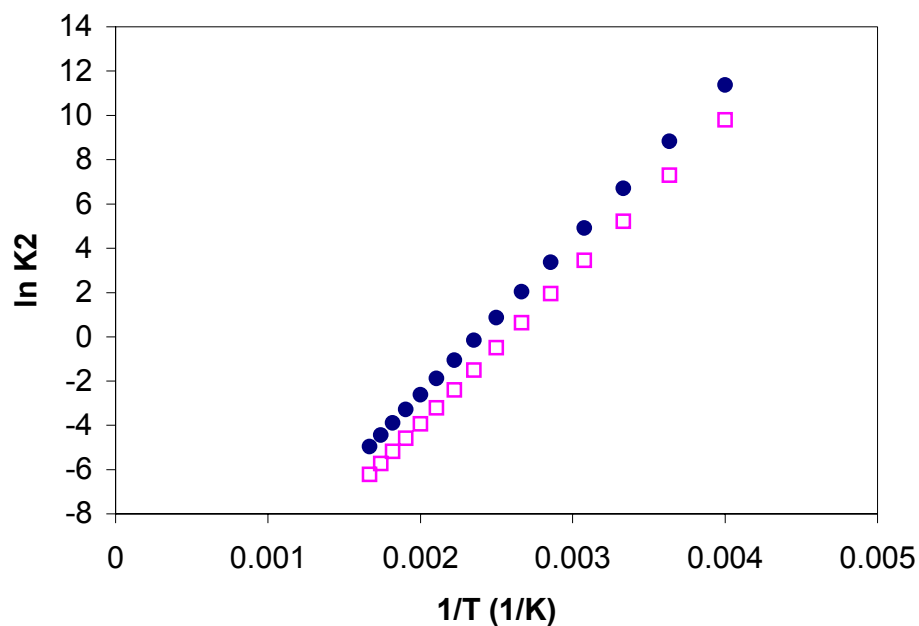


Figure 8. Butyric Acid Equation 2 Equilibrium Expressions from Gmehling et al. (●) and from This Work's B3LYP Calculations (□)